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Synthesis, Structure and Catalytic Studies of Palladium and Platinum Bissulfoxide Complexes

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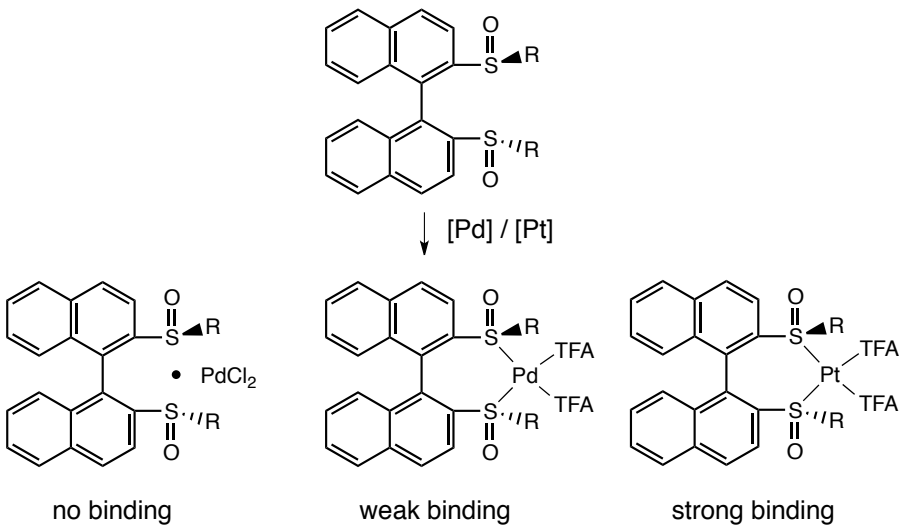
TOC graphic



Abstract

The bissulfoxide ligand, *p*-tolyl-binaso and its derivatives can be used to synthesize neutral and cationic palladium and platinum complexes. Various Pt bissulfoxide complexes could be made by using the precursor Pt{(M,S_S,S_S)-*p*-tolyl-binaso}Cl_2 (**5a**) and abstracting the chlorides with silver salts. The Pd analogue of this compound (**4**) could not be used in the same way. In this case, the sulfoxides appear to be very weakly coordinated and different methods to make stable Pd bissulfoxide complexes had to be found. The nature of the bonding in the synthesized compounds was studied through analysis of their IR and NMR spectra and X-ray crystal structures. These studies revealed that the *trans*-effect of other ligands in the complex is quite significant in determining the lability of the metal-sulfoxide bond. Some of the more stable platinum structures were then tested for their activity as catalysts in hydroboration and diboration reactions.

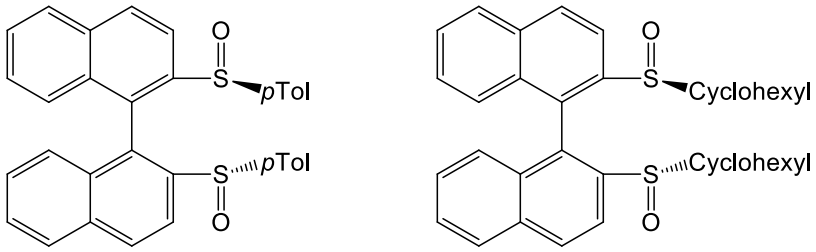
Introduction

The binding of sulfoxides with transition metals has been of interest for many years,[1-3] and numerous complexes with sulfoxide ligands, particularly dimethylsulfoxide (DMSO), are known and well characterized. It was observed very early on that sulfoxides were ambidentate in nature,[4] and depending on the metal and the steric environment, could bind through the lone pairs at sulfur or oxygen. Another interesting feature of sulfoxides is their chirality when dissymmetrically substituted. This makes them good candidates for the design of chiral ligands for enantioselective catalysis. The synthesis of enantiopure sulfoxides has been well studied,[5-14] and they generally show high optical stability. In contrast, only a few studies have demonstrated the use of chiral sulfoxide ligands in enantioselective catalysis, with excellent results in some cases.[15-20] Successful examples where the only chelating moieties are sulfoxides are still sporadic.[21-28]

Complexes of bissulfoxide ligands with palladium and platinum are known,[22, 29-34] but there are not many reports of them being used successfully in catalysis. The only examples reported are from the groups of Shibasaki[22] and White,[33] using palladium bissulfoxides. Following the success of bissulfoxide ligands developed in our laboratory in Rh catalysis,[23-25] we decided to study complexes of these ligands with palladium and platinum, with the goal of using them in catalysis. Herein, these complexes are presented along with some preliminary catalytic results.

For several of the complexes, it was possible to grow crystals suitable for X-ray crystallographic analysis. From these analyses we were able to more thoroughly understand the nature of the binding of these types of ligands, and also to see how the presence of other ligands in the complex affects the binding of bissulfoxides to these metals.[35]

The ligand used for most of the following studies was *p*-tolyl-binaso, **1**, previously developed and based on the well-known diphosphine ligand binap developed by Noyori (Chart 1).[36] A related ligand, cyclohexyl-binaso, **2**, was also used in the studies with palladium and platinum reported here and was synthesized as previously reported by us using DAG-(*S*)-cyclohexylsulfinate **3** (DAG = 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranosyl).[27]



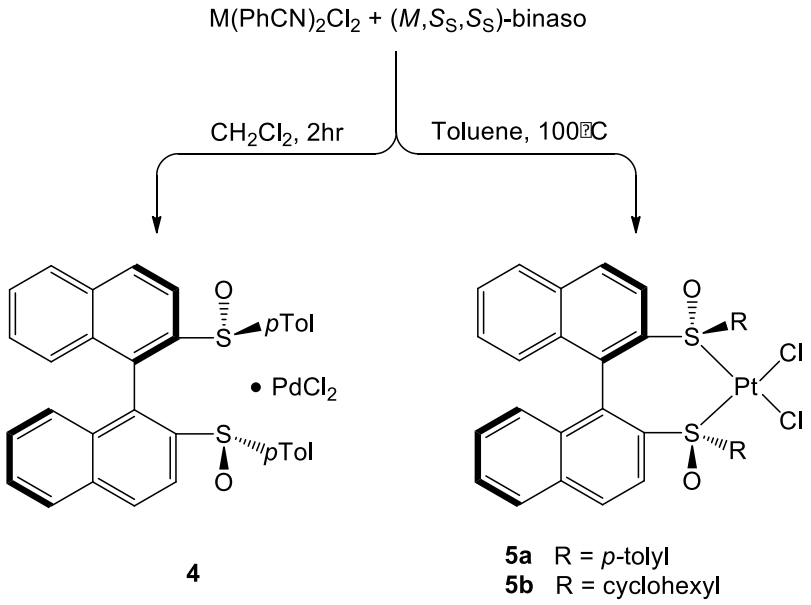
p-Tolyl binaso **1** Cyclohexyl-binaso **2**

Chart 1. *p*-tolyl-binaso **1** and Cyclohexyl-binaso **2** used in this study.

Results and Discussion

Our studies into palladium and platinum complexes with bissulfoxide ligands began with the discovery that we could make the monomeric dichloride complexes with **1** from $M(PhCN)_2Cl_2$ (where M = Pt or Pd). The two benzonitrile ligands were displaced by one equivalent of bissulfoxide ligand (scheme 1). The first results were achieved when the palladium complex, $Pd(PhCN)_2Cl_2$ (palladium(II) bis(benzonitrile)dichloride) was treated with a solution of the ligand in CH_2Cl_2. The solution changed color from yellow to red. However when the solvent was removed, the ^1H NMR spectrum of the resulting red solid

was the same as that of the free ligand. Nevertheless, the elemental analysis matched that predicted for Pd{(*M*,S_S,S_S)-*p*-tolyl-binaso}Cl_2 (**4**), and no benzonitrile was observed in the ^{1}H NMR spectrum. We postulate that in this case, the ligand forms weak interactions with the palladium, but is not properly bound. This was also observed by White and co-workers, where a bissulfoxide ligand appeared to form a complex with $Pd(OAc)_2$, but the ^{1}H NMR of the 'complex' and the free ligand were the same.[37]



4

5a R = *p*-tolyl
5b R = cyclohexyl

Scheme 1. Syntheses of $PdCl_2$·binaso and Pt(binaso)Cl_2

On the other hand, Pt{(*M*,S_S,S_S)-*p*-tolyl-binaso}Cl_2 (**5a**) and Pt{(*M*,S_S,S_S)cyclohexyl-binaso}Cl_2 (**5b**) were unequivocally formed. The ligand was heated with the Pt precursor in toluene, and a yellow solid precipitated out of solution. The ^{1}H NMR spectra of this solid showed that the signals of the bound ligand were shifted compared to the free ligand. The complex is very stable under N_2, and can be kept for months without any decomposition being observed. For further confirmation of its structure, an X-ray crystal structure of **5a** as its THF monosolvate was obtained (figure 1).

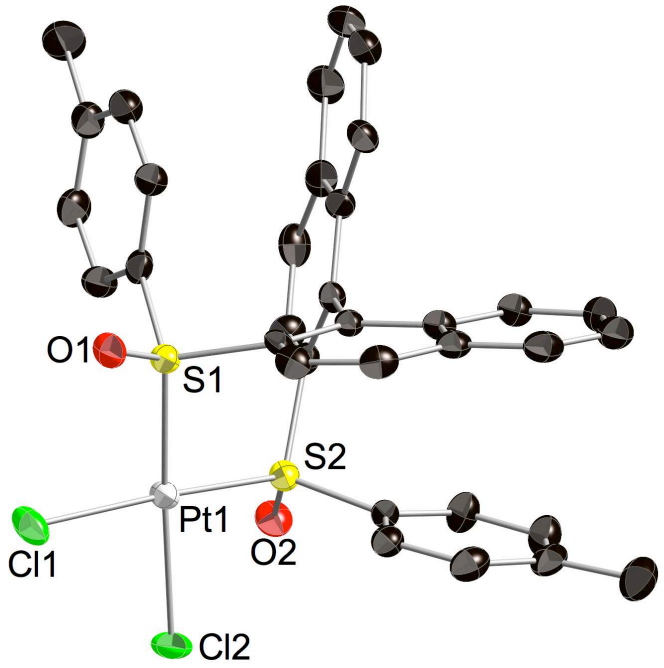


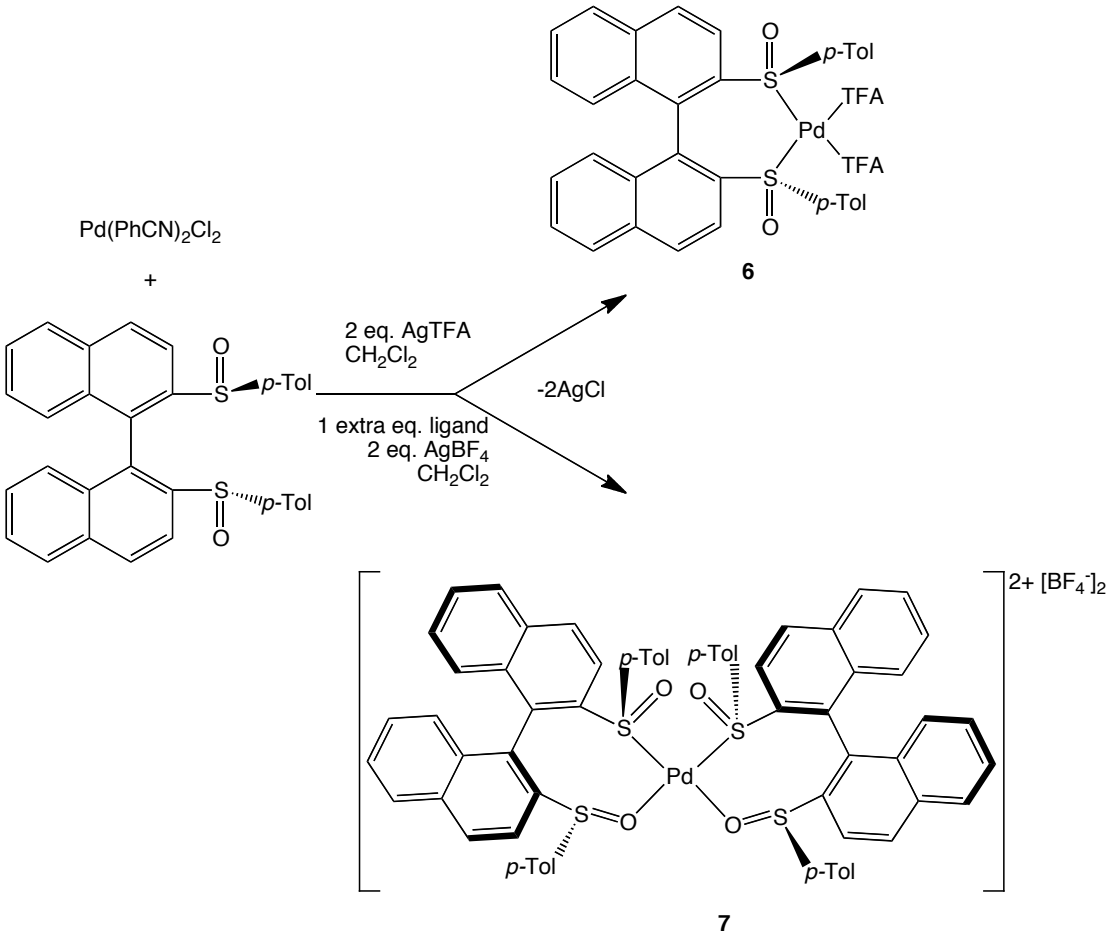
Figure. 1 The molecular structure of Pt{(M,S_S,S_S)-*p*-tolyl-binaso}Cl_2, **5a** (50% probability ellipsoids; hydrogen atoms have been omitted). Selected bond lengths (Å) and angles (°): Pt1-S1, 2.2496(9); Pt1-S2, 2.2527(9); Pt1-Cl1, 2.304(1); Pt1-Cl2, 2.315(1); S1-O1, 1.463(3); S2-O2, 1.467(3); Cl1-Pt1-Cl2, 88.72(4); S1-Pt1-S2, 98.46(3); Cl1-Pt1-S1, 88.62(4); Cl2-Pt1-S2, 85.48(3); S1-Pt1-Cl2, 169.41(4); S2-Pt1-Cl1, 170.21(4).

The crystal structure of **5a**.THF revealed discrete molecules with a *cis*-*S*,*S*-bidentate *p*-tolyl-binaso ligand and uniform Pt–Cl and Pt–S distances. The Pt-atom has a square planar coordination geometry with a small tetrahedral distortion. The coordinating atoms deviate by up to 0.19 Å from the mean plane defined by the four coordinated atoms and the Pt-atom and $\tau_4 = 0.14$. The τ_4 parameter has been used as a measure of the degree of distortion in square planar and tetrahedral geometries; $\tau_4 = 1$ for an ideal tetrahedron and 0 for an ideal square planar geometry,[38] although distortions of a square planar geometry in the direction of a square pyramid will also yield values of $\tau_4 > 0$. The exact cause of

the distortion is unclear, although steric interactions between the Cl-atoms and the nearby sulfoxide O-atoms could be a contributing factor (Cl···O = 3.063(3) and 3.153(3) Å; van der Waals radii sum = 3.27 Å). The conformational constraints imposed by the seven-membered metallacycle created by the *cis*-*S*,*S*-bidentate *p*-tolyl-binaso ligand would prevent the S=O groups rotating to a more congenial orientation. The dihedral angle between the mean planes through the two binaphthyl rings is 76.9(1)° and the preference for the rings in binapthyl systems to be nearly perpendicular to one another might impose further conformational strain on the metallacycle. The large bite angle of 98.46(3)º for the bissulfoxide ligand may also be contributing to the distortions as it compresses the remaining angles around the Pt-atom and the smaller of the two S–Pt–Cl angles corresponds with the longer of the two Cl···O distances.

It was found that palladium complexes with *p*-tolyl-binaso, where the ligand was clearly bound, could be formed using $Pd(PhCN)_2Cl_2$ in combination with silver salts, AgX (scheme 2). When 2 equivalents of AgTFA (TFA = trifluoroacetate) were added, Pd(*p*-tolyl-binaso)TFA_2 (**6**) was formed. The synthesis was possible with both diastereoisomers of the ligand. Crystals of complex **6** · $2Et_2O$, with the *cis*-*S*,*S*-bidentate (*P*,S_S,S_S)-*p*-tolyl-binaso ligand were grown, and an X-ray analysis was performed (figure 2). The C_2-symmetric complex shows the expected square planar coordination geometry, with no atom deviating from the plane defined by the four coordinated atoms and the Pd-atom by more than 0.008(4) Å and $\tau_4 = 0.06$. Nonetheless, some small angular distortions within the square plane are evident, again resulting from the large bite angle of 97.07(5)º for the bissulfoxide ligand necessitated by strain within the seven-membered metallacycle. The dihedral angle between the mean planes through the two binaphthyl

rings is 70.5(2)°. The absence of significant tetrahedral distortion of the square planar geometry in this case could be due to weaker steric interactions between the sulfoxide and triflate O-atoms (O···O = 2.870(5) Å) than between the Cl-atom and the sulfoxide O-atom in **5a**. Overall, the trifluoroacetate ligands modulate the electronic environment at the metal in such a way as to allow binaso to bind relatively tightly to palladium.



Scheme 2. Synthesis of palladium *p*-tolyl-binaso complexes **6** and **7** *via* abstraction of chlorides

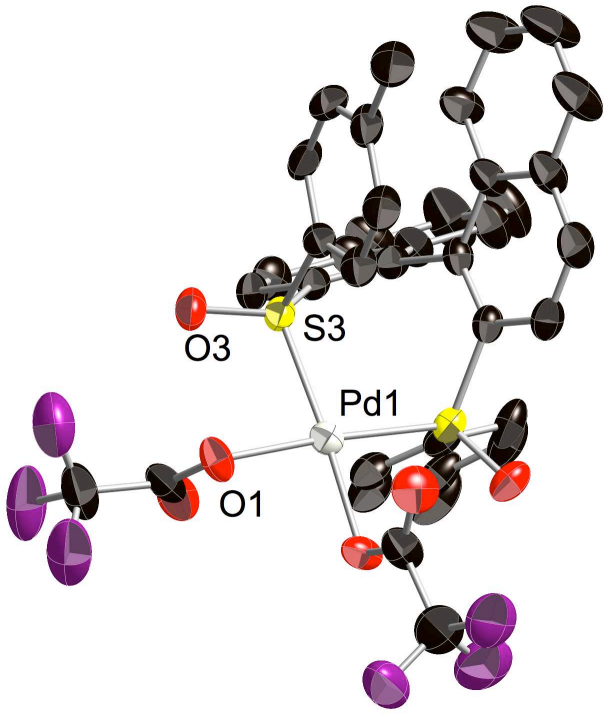


Figure 2. The molecular structure of Pd((*P*,S_S,S_S)-*p*-tolyl-binaso)TFA_2, **6** (50% probability ellipsoids; hydrogen atoms have been omitted). Selected bond lengths (Å) and angles (°): Pd1-S3, 2.243(1); Pd1-O1, 2.045(3); S3-O3, 1.460(3); S3-Pd1-S3', 97.07(5); O1-Pd1-O1', 88.6(2); S3-Pd1-O1, 87.19(9); O1-Pd1-S3', 175.72(9).

When $AgBF_4$ was added to the reaction instead of AgTFA, an interesting transformation occurred. Initially the reaction was carried out with one equivalent of $Pd(PhCN)_2Cl_2$, one equivalent of (*P*,S_S,S_S)-*p*-tolyl-binaso and two equivalents of $AgBF_4$. It was observed that the quantity of white solid, at the time believed to be AgCl, precipitating out of the reaction was greater than expected. The solid was filtered off, and an ^{1}H NMR analysis revealed it to be a mixture of AgCl and $Pd(PhCN)_4(BF4)_2$. The remaining red solution was also dried and was speculated to be Pd((*P*,S_S,S_S)-*p*-tolyl-binaso)$_2$(BF_4)$_2$ (**7**). ^{1}H NMR spectra showed the ligand to be desymmetrized and

supported this theory. The complex is fairly stable; when stored in the glovebox, no decomposition was observed after 1 year. Confirmation of the structure came from X-ray crystallographic analysis of crystals of the complex salt as its CH_2Cl_2 monosolvate, grown by layering a concentrated CH_2Cl_2 solution with pentane (figure 3).

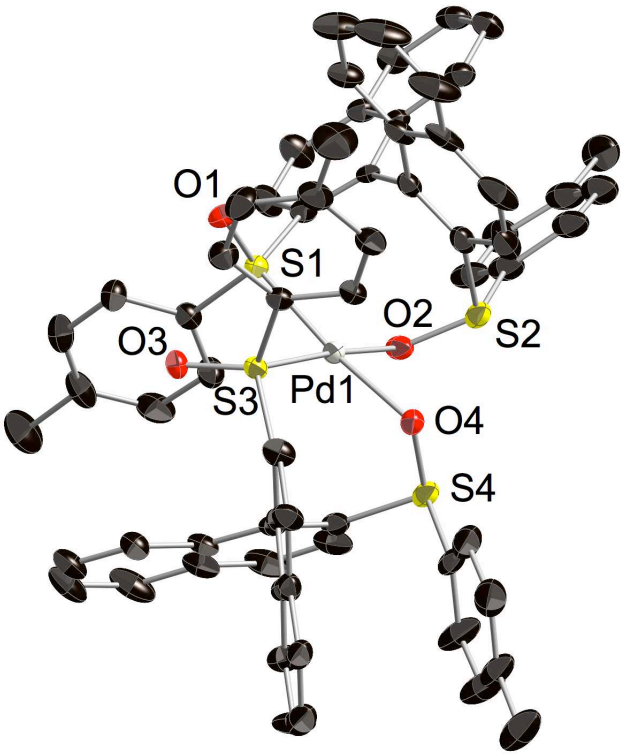


Figure 3. The structure of the cation of [Pd((*P*,S_S,S_S)-*p*-tol-binaso)$_2$][BF_4]$_2$, **7** (50% probability ellipsoids; hydrogen atoms have been omitted). Selected bond lengths (Å) and angles (°): Pd1-S1, 2.238(1); Pd1-S3, 2.2374(9); Pd1-O2, 2.086(3); Pd1-O4, 2.088(3); S1-O1, 1.457(3); S2-O2, 1.548(3); S3-O3, 1.451(3); S4-O4, 1.551(3); S1-Pd1-S3, 89.63(3); O2-Pd1-O4, 90.1(1); S1-Pd1-O2, 90.38(8); S3-Pd1-O4, 90.74(8); O2-Pd1-S3, 173.39(8); O4-Pd1-S1, 173.13(8).

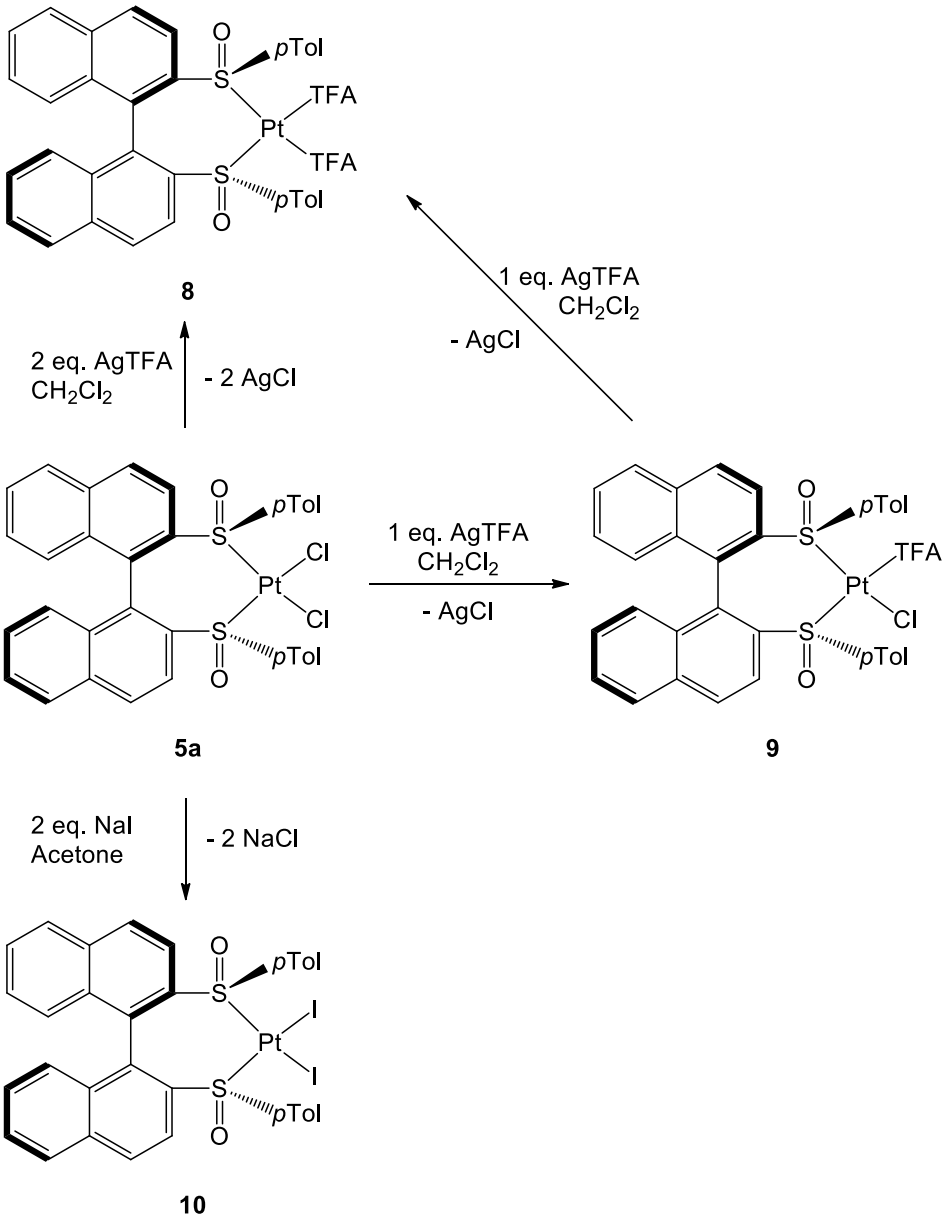
Each *p*-tolyl-binaso ligand in the complex cation of **7** $\cdot CH_2Cl_2$ coordinates in a *cis-S,O*-bidentate fashion to the Pd-atom and the coordinating S-atoms from the two ligands are also *cis*-positioned. To the best of our knowledge, this is the first example of a bissulfoxide ligand chelating simultaneously through S and O with a late transition metal. The Pd–S bond distances in **7** are not significantly different to those in **6**. The ambidentate binding modes of the *p*-tolyl-binaso ligands leads to expected differences in the S=O bond lengths, with an average of 1.454(4) Å for the S-bound sulfoxide group and a substantially longer 1.550(4) Å for the O-bound sulfoxide group. For comparison, the S=O bond length in the free ligand is intermediate at 1.491(2) Å.[39]

The Pd-atom has a slightly tetrahedrally distorted square planar coordination geometry, $\tau_4 = 0.10$, with the coordinating atoms deviating by up to 0.13 Å from the mean plane defined by the four coordinated atoms and the Pd-atom. This is despite the fact that *p*-tolyl-binaso forms an eight-membered metallacycle in this complex, which gives the ligands more flexibility to form the preferred 90º bite angles. The dihedral angles between the mean planes through the two pairs of binaphthyl rings are 83.1(2) and 85.7(1)°. These angles are closer to 90° than observed in all of the crystal structures reported here involving *S,S*-coordinated binaso ligands, which may further reflect the reduced strain inherent in the eight-membered metallacycle.

(P,S_S,S_S)-*p*-tolyl-binaso could only be used to make neutral complexes with palladium, no neutral platinum complexes were made cleanly with this ligand. In addition, only the (P,S_S,S_S)-ligand could be used to make complex **7**. When the reaction was carried out using one equivalent of $Pd(PhCN)_2Cl_2$, one equivalent of (P,S_S,S_S)-*p*-tolyl-binaso and one equivalents of $AgBF_4$, a complicated mixture of products was seen in the ^1H NMR

spectrum. We had hoped that the chloro-bridged dimer, with one ligand coordinated to each palladium, would form but this does not seem to be the case.

Returning to the investigation into the coordination of binaso to platinum, we were able to use complex **5a** as an entry point to a variety of other complexes (scheme 3). The dichloride complex (**5a**) could be treated with AgTFA in CH_2Cl_2 to abstract both chlorides resulting in complex **8**, which was very stable at room temperature inside the glovebox. Crystals suitable for X-ray analysis were grown by diffusion of THF into a CH_2Cl_2 solution of the complex (figure 4). The crystal structure of **8** shows complex molecules with a *cis*-*S*,*S*-bidentate (*P*,S_S,S_S)-*p*-tolyl-binaso ligand and two triflate ligands, one of which is disordered yielding two molecular conformations. One conformation, adopted by about 66% of the molecules, has a significant tetrahedral distortion of the Pt coordination environment with τ_4 = 0.19 and the coordinating atoms deviating by up to 0.21 Å from the mean plane defined by the four coordinated atoms and the Pd-atom. The remaining molecules actually have a slightly square pyramidal coordination geometry with τ_4 = 0.15 and the Pt-atom 0.104(1) Å from the plane defined by the four coordinating atoms. The bite angle of the bissulfoxide is slightly larger than in the Pd analogue [99.03(7)° for **8**, compared with 97.07(5)° for **6**] as a natural consequence of the slightly smaller covalent radius of Pt. The dihedral angle between the mean planes through the two binaphthyl rings is 79.7(3)°.



Scheme 3. Platinum complexes formed using **5a** as a precursor

When **5a** was treated with only one equivalent of AgTFA, only one chloride was abstracted and replaced by a TFA ligand to form complex **9**, which could be stored for months at room temperature under nitrogen. The ^{1}H NMR spectrum of this complex shows that the binaso ligand is desymmetrized by this transformation, and we assume the

structure to be that shown in scheme 3. Complex **9** could be reacted with another equivalent of AgTFA to cleanly give **8**.

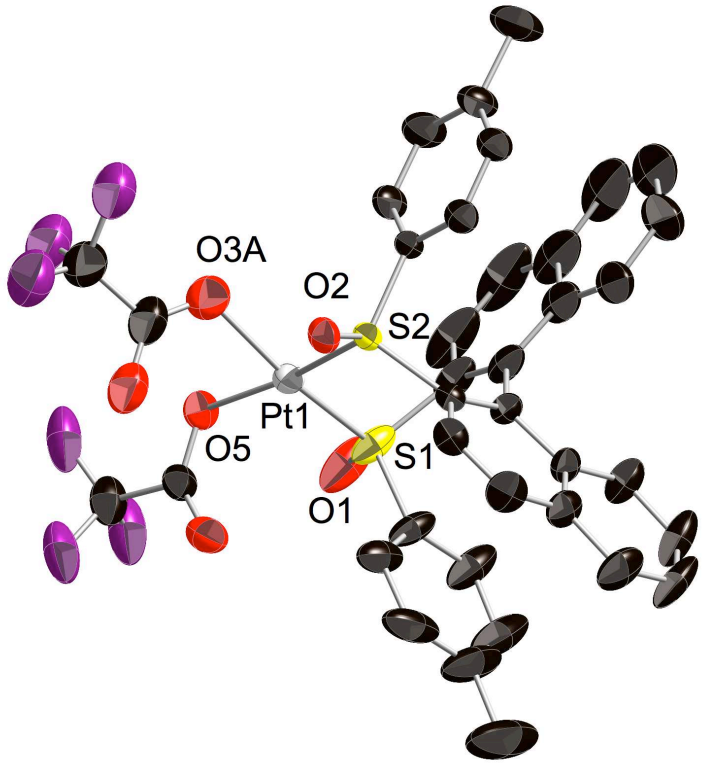


Figure 4. The molecular structure of Pt(M,S_S,S_S)-*p*-tol-binasoTFA$_2$, **8** (50% probability ellipsoids; hydrogen atoms and the minor positions of the atoms of the disordered triflate ligand (involving O3B) have been omitted). Selected bond lengths (Å) and angles (°): Pt-S1, 2.197(2); Pt1-S2, 2.239(1); Pt1-O3A, 2.063(8); Pt1-O3B, 2.063(9); Pt1-O5, 2.041(4); S1-O1, 1.465(5); S2-O2, 1.475(4); S1-Pt1-S2, 99.03(7); O3A-Pt1-O5, 82.7(3); O3B-Pt1-O5, 83.2(6); S1-Pt1-O5, 91.1(2); S2-Pt1-O5, 169.6(2); S1-Pt1-O3A, 163.9(3); S2-Pt1-O3A, 88.1(3); S1-Pt1-O3B, 168.7(5); S2-Pt1-O3B, 86.5(6).

Reacting **5a** with NaI in an acetone solution substituted the chloride ligands for iodides, giving an orange precipitate in less than 10 minutes. The orange solid was redissolved in

CH_2Cl_2 and layered with THF to give crystals of **10**·CH_2Cl_2 suitable for X-ray analysis (figure 5). Unlike complexes **8** and **9**, **10** decomposed in a matter of weeks when stored at room temperature under an inert atmosphere. Although only the halogen atoms have been exchanged, the crystal structures of **5a** and **10** are not isostructural, possibly because the two structures incorporate different solvent molecules. The molecules of **10** have crystallographic C_2-symmetry. The Pt–I bond distance in **10** is 2.5877(5) Å; this is almost 0.3 Å longer than the Pt-Cl bonds in **5a**. However, the Pt–I distance is not unusually long, in fact it is marginally shorter than the distances found in a similar coordination environment. The Cambridge Structural Database[40] contains details for 14 structures with a square planar PtI_2S_2 core and the range of Pt–I bond lengths for those complexes are 2.60-2.63 Å. The Pt-atom has a significantly tetrahedrally distorted square planar coordination geometry, $\tau_4 = 0.24$, with the coordinating atoms deviating by up to 0.36 Å from the mean plane defined by the four coordinated atoms and the Pt-atom. The distortions appear to be clearly a consequence of steric interactions between the I-atoms and the nearby sulfoxide O-atoms. The I···O distance of 3.353(5) Å is shorter than the van der Waals radii sum of 3.50 Å by a similar amount to that observed for the Cl···O separation in **5a**, but were the coordination geometry in **10** strictly square planar, the I···O distance would be even shorter. The dihedral angle between the mean planes through the two binaphthyl rings is 70.5(3)° and the bite angle of the *S*,*S*-bidentate ligand is 97.78(7)°. Both these values, particularly the dihedral angle, are a little smaller than the corresponding angles in **5a** and **8**, and may be related to the Pt–S bond in **10** being slightly longer than in the analogous chloride and TFA complexes (Table 1) as a consequence of the *trans*-effect, which will be discussed below.

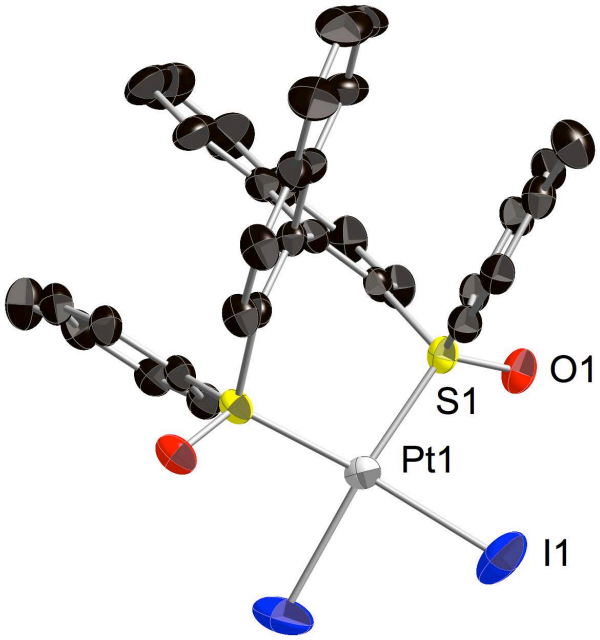
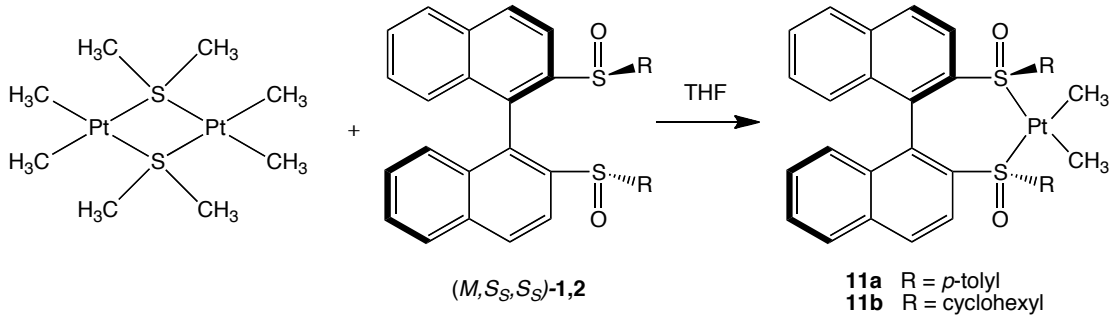


Figure 5. The molecular structure of Pt(M,S_S,S_S)-*p*-tol-binasolI_2, **10** (50% probability ellipsoids; hydrogen atoms have been omitted). Selected bond lengths (Å) and angles (°): Pt1-S1, 2.261(1); Pt1-I1, 2.5877(5); S1-O1, 1.466(4); S1-Pt1-S1', 97.78(7); I1-Pt1-I1', 88.75(3); S1-Pt1-I1, 89.09(4); S1-Pt1-I1', 162.91(3).

Starting from a different Pt precursor, namely [Pt(μ-SMe_2)Me_2], the dimethyl complexes incorporating bissulfoxides **1** and **2** were formed cleanly as shown in scheme 4. Crystals of the racemic dimethyl complex **11b** as its CH_2Cl_2 solvate were grown and an X-ray analysis performed (figure 6). The crystal structure revealed Pt–S bond lengths of 2.3075(6) and 2.3107(6) Å. These are the longest Pt–S bonds observed for any of the complexes described herein, but are consistent with three other structures containing the PtS_2Me_2 core listed in the Cambridge Structural Database (range 2.305-3.363 Å). Complex **11b** was also the least stable and had to be stored in the refrigerator, inside the glovebox, to avoid decomposition. Similar to **6**, the tetrahedral distortion of the square

planar coordination geometry is small. The coordinating atoms deviate by only up to 0.05 Å from the mean plane defined by the four coordinated atoms and the Pt-atom, while τ_4 = 0.09. Nonetheless, there are significant angular distortions within the square plane induced by the bite angle of the *S*,*S*-bidentate ligand of 97.41(2)°. The dihedral angle between the mean planes through the two binaphthyl rings is 72.47(7)°. The smaller degree of tetrahedral distortion of the coordination geometry correlates with a weaker steric interaction between the sulfoxide O-atoms and the methyl C-atoms than in complexes **5a**, and **10**. The O···C distances are 3.096(3) and 3.164(3) Å, which are only 0.12 and 0.06 Å, respectively, shorter than the sum of the van der Waals radii of these atoms.



Scheme 4. Synthesis of complexes **11a** and **11b**

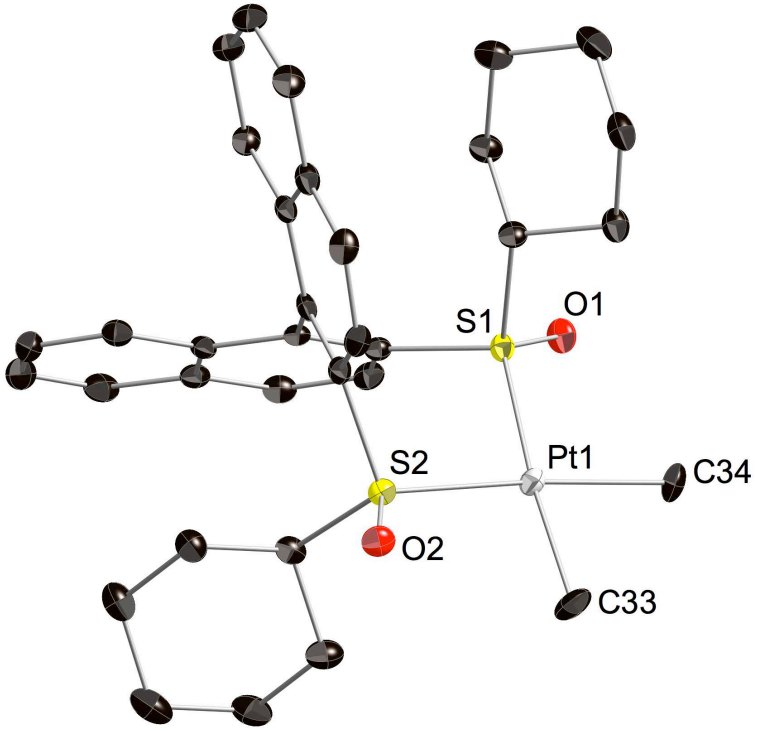
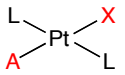


Figure 6. The molecular structure of Pt(cyclohexyl-binaso)$(Me)_2$, **11b** (50% probability ellipsoids; hydrogen atoms have been omitted). Selected bond lengths (Å) and angles (°): Pt1-S1, 2.3075(6); Pt1-S2, 2.3107(6); Pt1-C33, 2.071(3); Pt1-C34, 2.067(2); S1-O1, 1.4793(17); S2-O2, 1.4809(17); S1-Pt1-S2, 97.41(2); C33-Pt1-C34, 84.39(11); S1-Pt1-C33, 88.77(8); S2-Pt1-C34, 89.53(8); C33-Pt1-S2, 173.63(8); C34-Pt1-S1, 172.47(8).

It has long been known that there are two phenomena at play in square planar Pt complexes, where a ligand X, *trans* to another ligand A, affects the stability of the Pt-A bond (*trans*-influence) or the ease of substitution of A (kinetic *trans*-effect).[41, 42] It was verified experimentally that the labilizing effect (kinetic *trans*-effect) decreases in the following order:

$$X = C_2H_4 \sim CO > CN^- > R_3P \sim H^- > CH_3^- > C_6H_5^- > I^- > Br^- > Cl^- > NH_3 > OH^- > H_2O$$



It is believed that σ- and/or π-interactions are important for ligands displaying a strong kinetic *trans*-effect. Good σ-bonding between the p-orbital of the ligand X and the 6p orbitals of Pt stabilizes the transition state in the substitution of A for another ligand.[41] On the other hand, empty π* orbitals on the ligand X may assist the substitution reaction by accommodating electron density from the entering ligand built up on the metal center.

Studies of complexes of the general formula *trans*-$PtCl_2(L)(NH_3)$, where L was various σ-bonding ligands, led to the conclusion that the *trans*-influence closely mirrors the kinetic *trans*-effect in most cases.[41] Upon inspection of the Pt–S bond lengths (from the X-ray crystal structures) and the S=O bond IR frequencies of the neutral Pt complexes described herein (table 1), we observed a *trans*-influence in the following order:[43]

$$CH_3^- > I^- > Cl^- > TFA$$

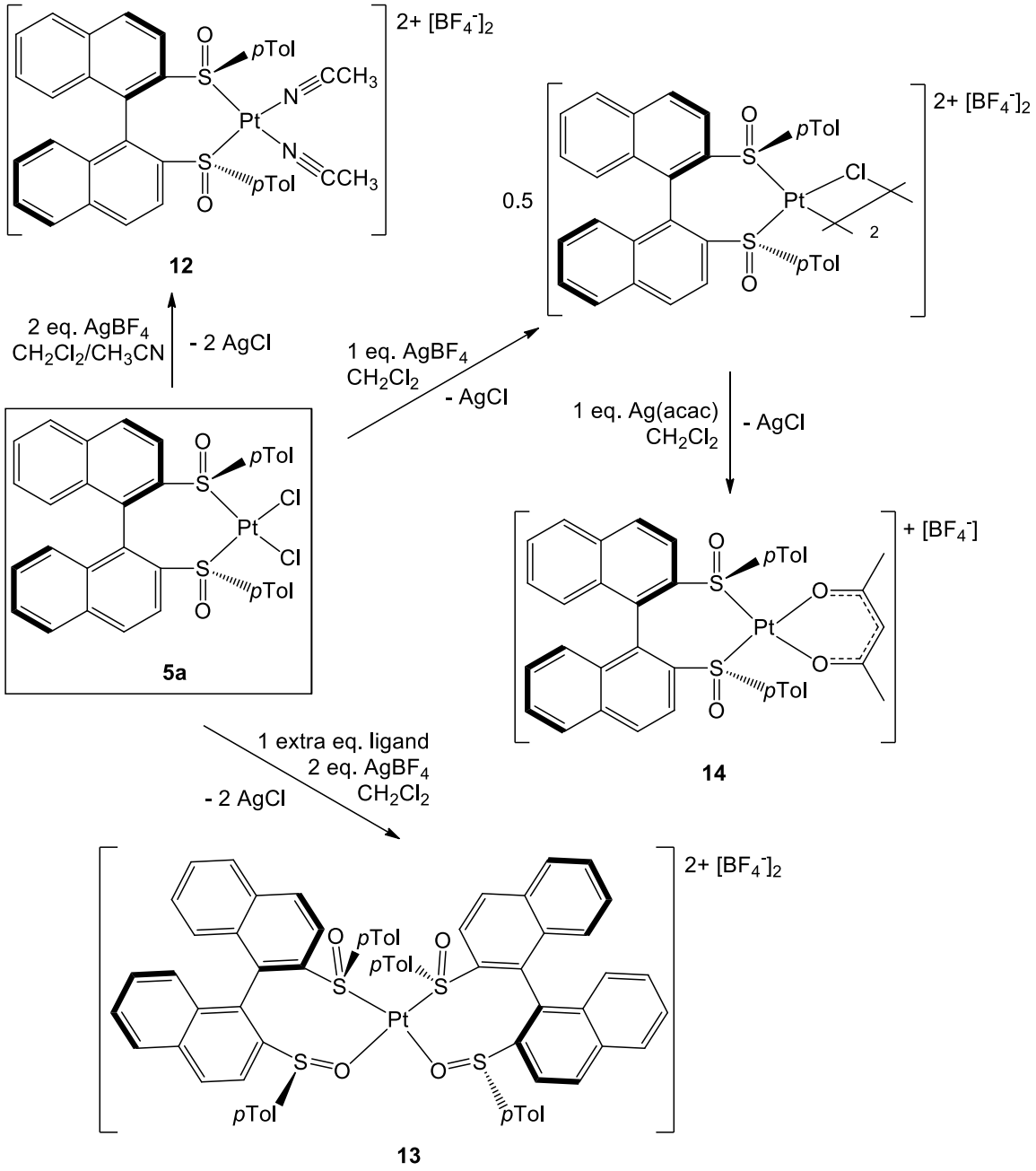
Table 1. Comparison of Pt–S bond lengths and IR frequency of S=O bond

Compound	*trans* Ligand	Av. Pt–S bond distances (Å)	υ(S=O) (cm^{-1})
Free binaso	N/A	N/A	1055.84
8	-TFA	2.218(2)	1177.33
5a	-Cl	2.251(1)	1136.83
10	-I	2.261(1)	1129.12
11b	$-CH_3$	2.3091(8)	1093.44

This is in agreement with what is stated in the literature for square planar Pt complexes[41, 42] and our own observations as to the stability of these complexes. The *trans*-influence and kinetic *trans*-effect are important to bear in mind when designing new complexes to synthesize or when predicting the behavior of these complexes in catalysis. Ligands with a strong *trans*-influence in the *trans* position to the sulfoxides might labilize the bissulfoxide during catalysis. If this were the case, the chiral ligand might not be chelating to the metal throughout the catalytic cycle.

Parallels can be drawn between the trends observed for the Pt complexes and those observed with the Pd complexes. Above we have seen that Cl^- appears to exert a stronger *trans*-influence on the bissulfoxide ligand than TFA in the neutral Pt complexes discussed. Similarly, we saw earlier that in the Pd-bissulfoxide dichloride complex (**4**), the binaso seemed to coordinate weakly, whereas the Pd-bissulfoxide TFA complex (**6**) was a stable, isolable compound.

In an extension of the complexation chemistry of these bissulfoxides with platinum, we synthesized various cationic Pt complexes employing **5a** as the starting material (scheme 5). When **5a** was treated with 2 equivalents of $AgBF_4$ in a solvent mixture of CH_2Cl_2 and CH_3CN, the chlorides were abstracted and replaced by two acetonitrile molecules to form complex **12**. The coordinated CH_3CN was clearly seen in the ^1H and ^{13}C NMR spectra.



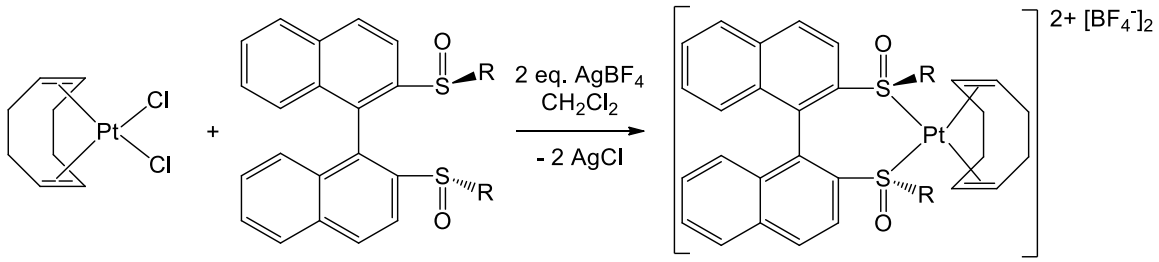
Scheme 5. Cationic platinum complexes made from **5a**

This complex was stable inside the glovebox and could be stored at room temperature. Similarly, complex **13** was formed by reacting **5a** with 2 equivalents of $AgBF_4$ and an extra equivalent of *p*-tolyl-binaso in a CH_2Cl_2 solution. We were not able to obtain a crystal of this complex to confirm the structure unambiguously, but spectroscopic

evidence points to an analogous structure to the Pd complex **7** (scheme 2). The ^{1}H NMR spectrum of **13** shows the binaso ligand to be desymmetrized, which suggests formation of the proposed structure.

When **5a** was treated with only 1 equivalent of $AgBF_4$, unlike in the Pd case, a chloro-bridged complex was formed. No crystals could be grown to confirm the structure, but an in-situ ^{1}H NMR spectrum after the first step of the reaction to form **14** showed the ligand to be still symmetric. Furthermore, there is a precedence for this type of chloro-bridged Pt dimers in the literature with phosphine ligands.[44,45] This intermediate then reacted cleanly with 1 equivalent of Ag(acac) (acac = acetylacetonate) to give the monocationic complex **14**. This complex was stable at room temperature under nitrogen and ^{1}H and ^{13}C NMR spectra revealed that both acac and binaso ligands were coordinated.

Finally, another group of cationic platinum complexes were made from the precursor $Pt(COD)Cl_2$ (COD = cyclooctadiene). It was found that upon treating the precursor with one equivalent of ligand and two equivalents of $AgBF_4$, the chlorides were abstracted and the ligand co-ordinated to Pt to produce the dicationic complexes **15a**, **b** and **c** (scheme 6). ^{1}H NMR spectra confirmed that both the bissulfoxide ligand and cyclooctadiene were coordinated in each case.



(M,S_S,S_S)-**1,2**
or (P,S_S,S_S)-**1**
L*

15a L* = (M,S_S,S_S)-**1**
15b L* = (M,S_S,S_S)-**2**
15c L* = (P,S_S,S_S)-**1**

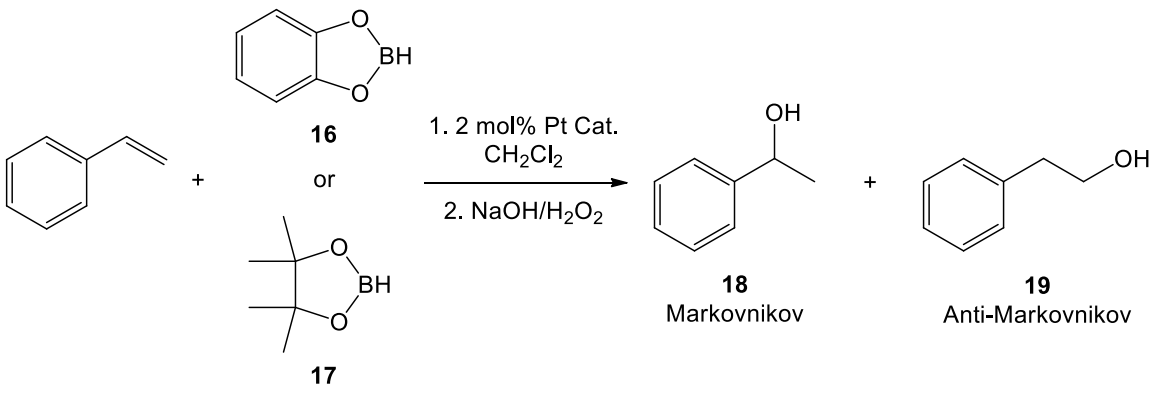
Scheme 6. Synthesis of [Pt(binaso)(COD)][BF_4]$_2$ complexes, **15a**, **b** and **c**.

Hydroboration

To evaluate some of our platinum-bissulfoxide complexes as possible catalysts in asymmetric transformations, we decided to initially focus on hydroboration and diboration reactions. Hydroboration reactions can be carried out non-catalytically, but the major product observed is the anti-Markovnikov addition product;[46] catalysts can be used to invert this selectivity. The catalytic version of this reaction has been most well-developed with rhodium catalysts.[47-60] There is very little in the current literature regarding the use of platinum in hydroboration reactions. There is only one example of catechol borane being used in the hydroboration of a terminal alkene with a platinum catalyst.[61] Other examples include the hydroboration of terminal alkenes with polyboranes,[62-64] and the hydroboration of allenes with pinacol borane.[65]

As can be seen from entry 1, when no catalyst is present there is no reaction. For this type of reaction the non-catalytic version usually requires heating to high temperatures to obtain any product.[47] **5a** was the first platinum complex tested in the hydroboration of styrene with catechol borane, **18**, but only a trace of product was observed. Abstracting the chlorides in the complex with silver salt first (entry 3 of table 2) failed to give the desired product. The cationic Pt complexes **15a**, **b** and **c** were then tested in the reaction **15a** and **c** gave moderate yields at -25°C.

Table 2. Screening of Pt complexes in hydroboration reactions



Entry	Catalyst	Borane	Temp (°C)	Yield[a] %	Ratio[b,c] 20:21
1	-	16	-20	0	-
2	**5a**	16	-20	trace	-
3	**5a**[d]	16	-20	0	-
4	**15a**	16	-25	55	4:1
5	**15c**	16	-25	38	2.6:1
6	**15a**	16	23	trace	-
7	**15c**	16	23	trace	-
8	**15b**	16	0	0	-
9	**15a**	17	23	90	1.2:1
10	**15c**	17	23	94	1.1:1
11	**15c**	17	-5	79	1:1
12	**15c**[e]	17	23	39	0.9:1
13	**15c**[f]	17	23	47	1.3:1
14	**15c**[g]	17	23	82	0.8:1
15	**15c**[h]	17	23	60	1.1:1

[a] Isolated yield after appropriate work-up and purification by column chromatography; [b] 18:19, Determined by GC; [c] Products containing stereocenters were racemic mixtures according to HPLC on chiral stationary phase; [d] Pt complex was reacted with 10 mol% AgOTf for 30 minutes and filtered prior to catalytic reaction; [e] Reaction carried out in THF; [f] Reaction carried out in ether; [g] Reaction carried out in acetone; [h] Reaction carried out in toluene.

Interestingly, when the temperature was raised to room temperature, only traces of product were obtained. **15a** gave the best selectivity observed in this study, with a 4:1 ratio of Markovnikov to anti-Markovnikov product being observed at -25°C (entry 4). **15b** did not give any product (entry 8).

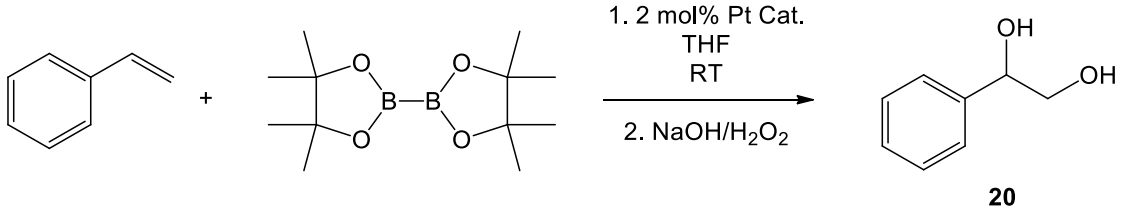
When the borane was changed to pinacol borane, the yields were dramatically improved and the reaction could be run at room temperature (entries 9 and 10), although the regioselectivity was decreased. Running the reaction at lower temperatures did not improve the selectivity with pinacol borane, and the yield was lower (entry 11). The reaction was screened with different solvents (entries 12-15), and it was found that the solvent affects both the yield and the selectivity of the reaction. THF and acetone gave higher selectivity for the anti-Markovnikov product.

For each of the reactions yielding enough isolable product, the mixture of primary and secondary alcohol were analysed by GC to give the ratio of these two alcohols. The *e.e.* of the secondary alcohol was determined using a GC column with a chiral stationary phase (Lipodex E). In each case the secondary alcohol was found to be racemic.

Diboration

Inspired by recent publications on Pt-catalyzed diborations, we tested some of our Pt complexes in the diboration of styrene by $B_2(pin)_2$ (table 3).[66,67] Diborations have been well developed with transition metal catalysts.[68-70] They are useful transformations for the introduction of new functional groups into a molecule. Obviously, if the reaction can be carried out enantioselectively, it is an efficient way to introduce chiral centers.

Table 3. Screening of Pt catalysts in the diboration reaction



entry	catalyst	Yield[a] %
1	**5a**	18
2[b]	**5a**	39
3	**8**	65
4	**14**	74
5	**13**	45
6	**11a**	80
7	**15a**	0
8	**15c**	0

[a] Isolated yield after quenching with $NaOH/H_2O_2$ and appropriate work-up and purification by column chromatography; [b] Products containing stereocenters were racemic mixtures according to HPLC on chiral stationary phase; [c] **5a** was first reacted with AgOTf in THF, then filtered and used in the catalytic reaction.

Most examples of diboration with platinum catalysts have been carried out with Pt(0),[71-76] although there are some examples using Pt(II).[77] This reaction was more convenient than the hydroboration reaction, as it could be run at room temperature with good results. Interestingly, **15a** and **15c** were not successful as catalysts in this reaction. This might indicate that the diboration goes through a different mechanism than the hydroboration reaction. Baker and co-workers showed that $PtCODCl_2$ was a good catalyst for diboration and proposed that the first step of the mechanism was reduction of Pt(II) to

Pt(0) by the diborane, as they observed R_2B-Cl by ^{11}B NMR.[77] This could explain why **15a** and **15c** do not catalyze the reaction. Both these complexes do not have any ligand that can be removed by transmetallation to the boron.

As can be seen in table 3, relatively good yields can be obtained with some of the platinum complexes in this reaction, particularly **14** and **11a**. We were hoping that the product would show some enantiomeric excess. Unfortunately, when analyzed by HPLC using chiral stationary phases (chiralcel OD-H), the product turned out to be racemic.

Summary

We have developed a family of new palladium and platinum complexes with the bissulfoxide ligands *p*-tolyl-binaso and cyclohexyl-binaso. These include a novel example of a bissulfoxide ligand binding simultaneously through S and O.

Through inspection of the X-ray crystal structures and IR spectra of the neutral, square planar Pt complexes, we were able to establish how the *trans*-influence of the other ligands affects the Pt-S binding strength of our bissulfoxides. This is important to bear in mind when designing Pt-binaso complexes to be used as catalysts. When the other ligands in the complex have a *trans*-influence on the Pt-S bond, the chiral bissulfoxide ligand may be made labile and not be fully chelating throughout the catalytic cycle. This could explain the lack of enantioselectivity we observed in the catalytic reactions tested. When extrapolating the trends seen for Pt to Pd, it appears likely that binaso and other chelating bissulfoxide ligands will have to be electronically altered in order for them to be coordinated more tightly to the palladium center.

It was also observed from the X-ray crystal structures that although the backbone and sulfoxide substituents are removed from the metal center, steric interactions between the sulfoxide O-atoms and the other coordinated ligands lead to various degrees of distortion, usually towards tetrahedral, of the square planar coordination geometry. The observation that the S=O moiety plays an important role in determining the structures of the sulfoxide-metal complexes is not surprising, as we have seen similar results in rhodium complexes with bissulfoxide ligands.[28]

Selected Pt complexes were tested in the hydroboration and diboration of styrene. **15a** gave selectivities of up to 4:1 of the Markovnikov product vs. the anti-Markovnikov product with catechol borane. Better yields were obtained with pinacol borane, but the selectivities were lower. In the diborations, **11a** was found to be the best catalyst, with **15a** and **15c** giving no product at all. Work is ongoing to find new catalytic applications for these complexes, and to try to reach a more thorough understanding of the nature of the binding of these ligands in respective catalytic cycles with palladium and platinum catalysts.

Associated Content

Supporting Information: Detailed descriptions of experimental procedures and spectroscopic data of the compounds described. CIF files giving crystal structure data for complexes **5a**, **6**, **7**, **8**, **10** and **11b**. This material is available free of charge via the internet at http://pubs.acs.org.

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